

Research Article

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Alkali Lignin Catalytic Hydrogenolysis with Biofuel Production

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Abstract: In this paper synthesized palladium (Pd)-containing catalysts were used in the hydrogenolysis of lignin in the presence of a hydrogen donor solvent, i-propanol, to obtain liquid fuel components. A study of the influence of the catalyst support nature, catalyst preparation method and supercritical solvent nature on the lignin depolymerization was completed. It was found that the use of Pd-containing catalysts results in the formation of aromatic compounds (mainly benzene and toluene) for both supercritical solvents used (i-propanol and CO₂). The maximum conversion of lignin (50 %) was achieved when the supercritical i-propanol was used and maximum selectivity to aromatics (over 70 %) was observed in the presence of the Pd-containing catalyst synthesized by hydrothermal deposition on the polymeric matrix of hyper-crosslinked polystyrene.

Keywords: lignin; hydrogenolysis; catalyst; biofuel; supercritical solvent.

Abbreviations

HPS hypercrosslinked polystyrene, GSMS Gas Chromatography Mass-Spectrometry, THF tetrahydrofuran.

1 Introduction

Lignin is very difficult to process due to its complex nature and instability, consisting of irreversible changes in the properties of the polymer during thermal or chemical treatment. Currently, lignin is used as a low-grade boiler

fuel [1]. However, the chemical structure of lignin suggests that it can be a good source of chemicals when broken down into lower molecular weight units [2]. Based on a literature review it can be concluded that most studies are based on the hydrogenolysis of model lignin compounds (anisole [3-8], catechol [6, 9], guaiacol [6,7, 10,11]); however, the process of lignin depolymerization is more complex and is not described by the mechanism of model compounds conversion. The majority of research on lignin processing is focused on its thermal degradation (i.e. slow and fast pyrolysis and gasification) [12, 13]. Besides the valuable combustible gaseous products, thermal methods lead to the formation of so-called bio-oils, i.e. complex mixtures containing phenolic derivatives, aromatic hydrocarbons, olefins, etc. However, the direct use of bio-oil is not possible due to the high oxygen content and pure fuel properties (high density, high ash content, low heat value) [13]. Currently, there is a growing interest in the combined processes of conversion of lignin into liquid fuel including the simultaneous depolymerization and hydrogenation [14, 15]. New methods of synthesis of catalytic systems, active and stable both in the process of solvolysis and in the process of hydrogenation, have been developed in order to increase the conversion of the substrate and the yield of important chemical compounds. Catalytic systems such as Ni / DeAl-beta [16], Zn-Ga [17], Ru/C [18], Ru/SiC [19, 20], Ru/Al₂O₃ [21], NiMo/Al₂O₃ [22, 23], containing Pt on mesoporous molecular sieves MCM-41 with various Al content [24] are used to convert lignin into liquefied fuels. Approaches to lignin processing are based on reactions of rapid thermal processing [25, 26], hydrogenolysis [27, 28], liquefaction in supercritical media [29] and in the presence of oxidants [30, 31]. The destruction of lignin occurs more effectively when using combined methods, such as catalytic hydrogenolysis in supercritical water [28] or thermochemical solvolysis in formic acid, which serve as a hydrogen donor [32]. Hydrogenolysis is a very well known reaction in which carbon-carbon or carbon-heteroatomic bonds are cleaved, usually in the presence of a homogeneous or heterogeneous catalyst. These processes are effectively used to reduce the oxygen content

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of lignocellulose components and their derivatives. Reductive valorization of lignocellulose biomass and its relative molecular derivatives is usually carried out in the presence of a solvent to limit their thermal decomposition [27, 28]. As a consequence, due to the well-known poor solubility of H_2 in most solvents, hydrogenolysis processes require the direct use of high-pressure molecular hydrogen with all the drawbacks that this entails, including purchase, transportation, expensive infrastructure, and safety hazards. Simple organic molecules provide an acceptable green alternative to the direct use of molecular H_2 in reduction processes. Catalytic hydrogenolysis uses solvent-derived H-donor molecules to prevent safety problems with high-pressure hydrogen and explosive gas [33]. In 2012 Rinaldi and his colleagues first reported the use of a bimetallic catalyst RANEY® Ni in H-transport reactions of lignin model molecules. 2-propanol was used as a reaction solvent and hydrogen source and 32 model substrates were studied at temperatures from 80 to 120 °C for 3 hours. The results indicated that the Ni-catalyst RANEY® demonstrates high performance under hydrogenolysis conditions and good stability during regeneration [34, 35]. Since most of the research is aimed at the processing of lignin model compounds, the process of catalytic conversion of lignin isolated from raw plant materials is an important task. In this paper, we propose the use of palladium-based catalysts deposited on various carriers, since palladium has shown itself to be an active and selective catalyst in hydrogenation processes in our previous studies [36, 37] and the novel hydrothermal route for the catalyst preparation was used for lignin processing. The synthesized catalysts were tested in lignin hydrogenolysis in supercritical conditions in order to enhance the process efficiency. Two types of supercritical solvents i-propanol and CO_2 were used in this work.

2 Experimental

2.1 Pd catalyst preparation by impregnation

The hypercrosslinked polystyrene (HPS, MN-270, Purolight Inc., UK) or microporous alumina (Al_2O_3 , Neva Reactive, Russia) with a mean particle size of 80 μm was first washed with distilled water and acetone (chemical grade, ReaChim, Russia) and dried under vacuum. Then it was treated with a solution of the calculated amount (5 wt. % of metal) of metal precursor sodium tetrachloropalladate (chemical grade, Sigma-Aldrich, USA) in a complex solvent consisting of tetrahydrofuran (chemical grade,

ReaChim, Russia), methanol (chemical grade, ReaChim, Russia) and distilled water at room temperature for 10 minutes. Then the resulting catalysts were dried for 40 minutes at 80 °C and washed with an aqueous solution of sodium bicarbonate (chemical grade, ReaChim, Russia) and distilled water until there was no chloride-anion in the scouring waters. The washed catalysts were dried for 90 minutes at 80 °C and reduced at 300 °C by hydrogen for 3 hours. The resulting catalysts were signed as 5%-Pd/HPS and 5%-Pd/ Al_2O_3 .

2.2 Hydrothermal Pd deposition

Pd-containing catalyst synthesis by hydrothermal deposition was performed in a stainless steel high-pressure reactor Parr-4307 (Parr Instrument, USA). 1 g of HPS (MN-270, Purolight Inc., UK) was first washed with acetone (chemical grade, ReaChim, Russia) and dried at 70 °C. The calculated amount of sodium tetrachloropalladate (chemical grade, Sigma-Aldrich, USA) (5 wt. % of metal), 0.1 g of sodium bicarbonate (chemical grade, ReaChim, Russia) and 15 mL of distilled water were placed into the reactor which was then sealed and purged with nitrogen, heated up to 200 °C under 6.0 MPa of nitrogen pressure and maintained for 15 minutes. After the synthesis the mixture was cooled to room temperature, filtered and washed with 10 mL of distilled water. The resulting catalyst was signed as 5%-Pd/HPS-HT.

2.3 Lignin isolation procedure

The extraction of alkali-lignin from spruce sawdust (Tver Region, Russia) was carried out under laboratory conditions. First, the sawdust was crushed and treated with sulfuric acid (chemical grade, ReaChim, Russia) for hydrolysis of hemicelluloses. Then it was washed with distilled water and boiled in a 2n NaOH (chemical grade, ReaChim, Russia) solution for 3 hours, then the residue of lignin was filtered using a Buchner funnel and dried at a temperature of 102 °C.

2.4 Lignin hydrogenolysis process in supercritical propanol-2

The hydrogenolysis process of the isolated lignin was carried out in a six-cell reactor Parr Series 5000 Multiple Reactor System (Parr Instrument, USA), which allows six experiments to be carried out in parallel under different

conditions. First, 1 g of lignin, 30 ml of i-propanol (chemical grade, ReaChim, Russia) and the calculated amount of catalyst were introduced into the cell. Then the reactor was sealed and purged, first with nitrogen and then with hydrogen by successive opening and closing of valves. Then the necessary operating pressure of hydrogen and temperature were set. The process was carried out with continuous stirring (1700 rpm). Intensive mixing eliminates the influence of external factors on the studied process. The experiment was conducted for 2 hours under the following conditions: temperature 300 °C, partial H₂ pressure 3 MPa and process pressure after the heating 8.9 MPa. The process conditions used in the experiments indicate the supercritical state of i-propanol was reached [38].

2.5 Lignin hydrogenolysis process in supercritical CO₂

The hydrogenolysis process of the isolated lignin was carried out in supercritical carbon dioxide in a high-pressure reactor Parr-4570 (Parr Instrument, USA) under the following conditions: 1 g of lignin, 30 mL of i-propanol (chemical grade, ReaChim, Russia) as co-solvent and 0.1 g of catalyst were added into the reactor. The reactor was sealed and purged with CO₂ at a pressure of 7.5 MPa. Then the reactor was heated to 150 °C and hydrogen with a partial pressure of 3.0 MPa was fed into it. The final pressure achieved was 13.0 MPa. The process was carried out with continuous stirring (750 rpm) and the experiment was conducted for 3 hours.

2.6 Liquid phase analysis

In all experiments sampling took place after the reaction in order to maintain the phase equilibrium. The analysis of the liquid phase samples was performed using a GC-2010 chromatograph and GCMS-QP2010S mass spectrometer (SHIMADZU, Japan), with the following conditions; duration 25 minutes, initial column temperature of 150 °C was maintained for 5 minutes then the temperature was increased to 250 °C with the heating rate 5°K/min; injector temperature: 280°C; automatic split; pressure of He 53.6 kPa; common stream of He 81.5 ml/min; linear gas velocity 36.3 cm³/s; chromatographic column type HP-1MS: L = 30 m; d = 0.25 mm; film thickness 0.25 μm; ion source temperature: 260 °C; interface temperature: 280 °C; scanning mode 10 up to 800 m/z; scanning rate: 1666; electron-impact ionization.

Table 1: Results of the lignin hydrogenolysis over Pd-containing catalysts in supercritical i-propanol at 300 °C.

Catalyst	Selectivity %		Lignin conversion after 3 h, %
	to aromatics	to phenols	
5%-Pd/Al ₂ O ₃	9.4	0	18.7
5%-Pd/HPS	36.0	10.5	37.5
5%-Pd/HPS-HT	74.0	5.1	50.0

3 Results and Discussion

3.1 The influence of support and catalyst synthesis method on the lignin hydrogenolysis

The process of lignin hydrogenolysis using catalytic systems synthesized by the impregnation method was carried out in i-propanol. The results of the process in the presence of Pd-containing catalysts supported on HPS and alumina are presented in Table 1.

It can be seen that the alumina-based catalyst provides no more than 20 % conversion (calculated according to Eq. 1) after 3 hours of reaction. This value is in agreement with the literature data obtained for the reductive depolymerization of alkali lignin in the presence of an alumina-based catalyst [39].

$$\tilde{N} = \frac{m_r}{m_l + m_c} \cdot 100\%, \quad (1)$$

where C – lignin conversion, m_r – a mass of solid residue after the process, m_l – initial mass of lignin, m_c – a mass of catalyst.

The HPS-based catalyst, in contrast, showed higher activity in lignin hydrogenolysis in i-propanol allowing almost 40 % conversion after 3 hours. It has been discussed in the literature that HPS-based catalysts provide high activity because of their high surface area and prevent active phase particle aggregation during the reaction [40].

The product composition analysis showed that in the presence of alumina-based catalyst depolymerization resulted in the formation of 2-phenoxy-1-phenyl ethanol, guaiacylglycerol-β-guaiacylether, diphenyl ether etc. No phenolic compounds and negligible aromatics (mainly benzene and toluene) were obtained. The selectivity to the valorized aromatics (calculated according to Eq. 2) did not exceed 10 %. It should be noted that the data presented by

Bouxin et al. [39] also showed low selectivity to phenols (phenol, methyl phenol, catechol), however, no aromatic compounds were obtained.

$$S = \frac{A_i}{\sum_{i=1}^n A_i} \cdot 100\%, \quad (2)$$

where S – selectivity, A_i – peak area of the product on the chromatogram, $\sum A_i$ – a sum of peak areas of all obtained products on the chromatogram.

The use of a HPS-based catalyst led to the formation of phenolic and aromatic compounds. The maximum selectivity to phenols (about 30 %) was observed after 1.5 hours of the process; however, the lignin conversion was not higher than 10 %. Further hydrogenolysis resulted in a decrease in phenol yield and the formation of benzene due to the hydrodeoxygenation activity of palladium. The final selectivity to benzene was found to be 36 %.

The 5%-Pd/HPS-HT catalyst, synthesized by the hydrothermal method, was chosen for the experiment as it showed high activity on supercritical deoxygenation of fatty acids [41, 42]. It is interesting to note that the catalyst synthesized by hydrothermal deposition showed higher activity in lignin depolymerization compared to the one synthesized by impregnation (see Table 1) and a lignin conversion of 50 % was achieved within 3 hours. The 5%-Pd/HPS-HT catalyst showed high selectivity to aromatic formation (over 70%) indicating the behavior of deoxygenation reactions. It should be noted that the literature data on catalytic lignin depolymerization in the presence of hydrogen for Pd-containing catalysts showed the preferential formation of phenols [43, 44]. The formation of aromatics in this study can be explained by the higher activity of HPS-based catalysts related to the higher surface area.

3.2 Supercritical solvent effect on lignin hydrogenolysis

Based on the results obtained the 5%-Pd/HPS-HT catalyst synthesized by the hydrothermal method was chosen for the experiments. During the experiment in the absence of supercritical CO_2 the following compounds were obtained: benzene, toluene, phenylpropane, phenol, cresol, and propyl phenyl ether (Figure 1). The maximum selectivity to benzene, 34 %, is achieved in 3 hours. The maximum selectivity of phenol – 17 %, is achieved in 1 hour, and

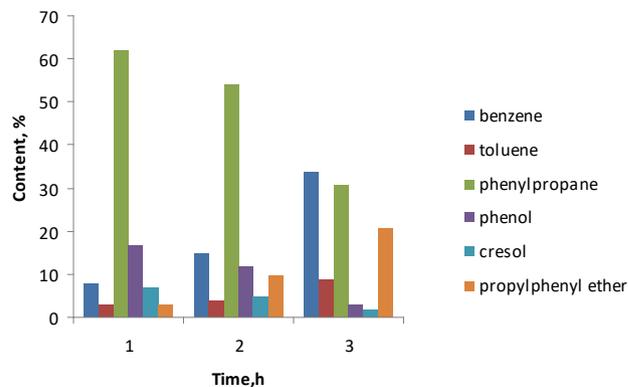


Figure 1: Liquid products distribution after lignin hydrogenolysis over 5%-Pd/HPS-HT catalysts in i-propanol at 150°C.

then its concentration decreased. High concentrations of phenylpropane were also observed in the first hours of the reaction (62 and 54 % for 1 and 2 hours respectively).

During the experiment in the presence of supercritical CO_2 only 30 % conversion of lignin was achieved within 3 hours due to the decrease in the reaction temperature compared to the experiments in i-propanol. The composition of the liquid phase was similar to that obtained in the experiment in the absence of supercritical CO_2 . It can be seen from Figure 2 that the formation of a large amount of phenylpropane (over 70 %) was observed within the first hours of the experiment. When the reaction time was increased the decrease in the phenylpropane selectivity was observed with the formation of benzene. The maximum selectivity to benzene was found to be 26 % in 3 hours. The maximum selectivity to phenol, 12 %, was observed after 1 hour of the reaction, however, the lignin conversion was less than 10 %.

The stability of the polymeric matrix at the temperature of the experiment was investigated using the thermogravimetry method. Thermal degradation of the polymer matrix of hypercrosslinked polystyrene occurs at temperatures above 450 °C. Catalytic systems have been studied in five consecutive cycles in which the activity of catalytic systems decreases slightly. This can be associated with a decrease in the total surface area probably due to the adsorption of reaction products in the pores of catalytic systems.

3.3 Catalyst characterization results

Physical and chemical studies of the synthesized catalytic systems were carried out (Table 2). In the study of the

Table 2: Physicochemical characteristics of catalysts.

Catalyst	$S_{\text{BET}}, \text{m}^2/\text{g}$	$S_{\text{t-plot}}, \text{m}^2/\text{g}$		Binding energy, eV	Metal state
		macropores	micropores		
HPS	1370	900	450	-	-
5%-Pd/HPS	705.0	75	630	335.0 (77.5 %) 337.4 (22.5 %)	Pd(0) PdO
5%-Pd/HPS (HT)	1230	630	680	335.0 (63.7 %) 337.4 (36.3 %)	Pd(0) PdO
Al_2O_3	108	85	24	-	-
5%-Pd/ Al_2O_3	86	32	57	-	Pd(0) PdO

HT - catalyst synthesized by hydrothermal method

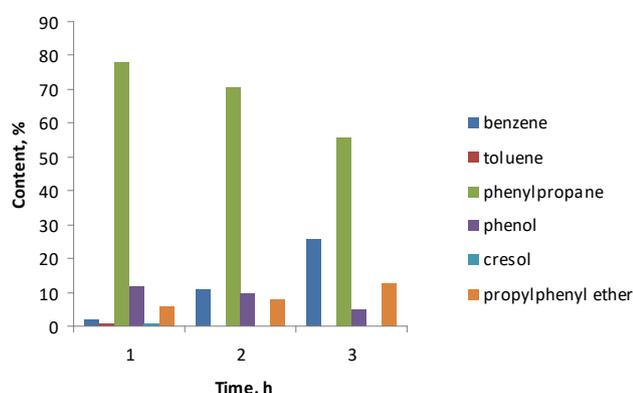


Figure 2: Liquid products distribution after lignin hydrogenolysis over 5% Pd/HPS HT catalysts in supercritical CO₂ in the presence of i-propanol at 150 °C.

surface area of the catalytic systems synthesized by impregnation a significant decrease in the surface area (and in particular the surface area of micropores) was observed. This may be due to pore blockage by the metal-containing particles during the synthesis. For the catalyst synthesized by the hydrothermal method, no noticeable decrease in the surface area was observed. However, the decrease in the micropore surface area was noted due to the pore restructuration, as shown in [41].

XPS study of the catalysts showed that for the HPS-based catalysts carbon was the main component on the catalyst surface (~80 at. %). Trace amounts of N, Cl, Si, and S (0.5, 0.9, 0.9 and 0.5 at. % respectively), which are the natural contaminants, were also observed on the surface of catalyst synthesized by impregnation. It is noteworthy that no surface contaminants were observed on the surface of the catalyst synthesized by hydrothermal deposition which indicates the removal of impurities during the synthesis. The surface concentration of the

active metal was 3.0 at. % for 5%-Pd/HPS and 4.3 at. % for 5%-Pd/HPS-HT.

For the alumina-based catalyst the main surface elements observed were Al (41 at. %) and O (52 at. %), and traces amount of natural contaminants (N, Cl, and S of 0.3, 0.8, and 0.2 at. % respectively). The surface concentration of the active metal was 2.7 at. % for 5%-Pd/ Al_2O_3 .

XPS analysis also showed that for all studied catalysts the composition of the active phase was mainly Pd (0) and PdO. For the catalysts synthesized by the impregnation method, a trace amount of palladium chloride (a metal precursor) was observed on the catalyst surface indicating the partial decomposition of the metal precursor during the synthesis and reduction of the catalysts.

4 Conclusions

Hydrogenolysis of lignin in the presence of Pd-containing catalysts was studied. The influence of catalyst support, catalyst synthesis method and the solvent on the lignin conversion and product yield was investigated. The experiments showed that the Pd-containing catalyst supported on HPS showed high effectiveness in lignin conversion allowing the aromatic compounds to be obtained. The maximum lignin conversion (50 %) and benzene yield (34 %) were obtained in i-propanol medium while using a 5%-Pd/HPS-HT catalyst synthesized by the hydrothermal method.

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